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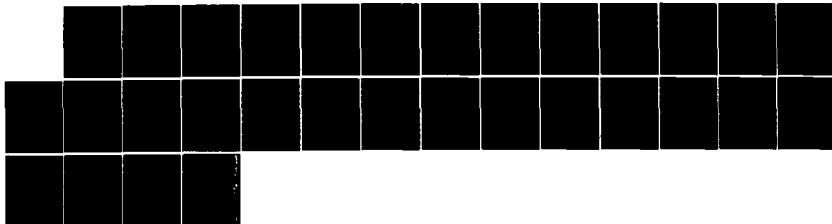
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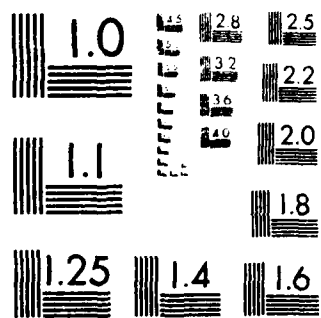
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SPECTROSCOPIC RESEARCH AT HIGH
PRESSURE AND VARIABLE TEMPERATURE

by

W. F. SHERMAN

June 1984

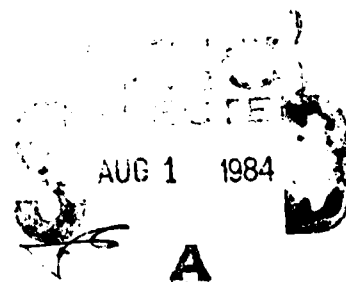
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Work concentrated on the use of spectroscopic techniques to probe material held under high pressure at various temperatures with the objective of improving understanding of intermolecular forces and the material properties which depend on them. Included in the work was the development of high pressure optical cells to extend capabilities to high temperatures (1,500K) and investigations of the use of non-spectroscopic probes.		

Summary

New high pressure spectroscopic cells have been developed to extend the range of the variable temperature high pressure studies that are currently the main interest of the group. During the period of this contract a total of 55 papers has been produced by our research group. The titles and references for these papers are listed at the end of this report and the scientific significance of some of this work is outlined within the report.

Significant contributions to our understanding of intermolecular forces, molecular motion in condensed phases and phase change mechanisms have been made during the course of the work reported here.



A-1

Key words

High pressure, variable temperature, Raman, infrared, far infrared, optical cells, intermolecular forces, molecular motion, phase changes.

As agreed with Dr. S H Lehnigk (ERO London) this report relies heavily on the list of published material that is included at the end. Two copies of each item on that list is included with the top copy of this report.

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1. Introduction

In principle, spectroscopic data from materials subjected to high pressures can be recorded for a wide range of different sample temperatures. In practice, most high pressure work is carried out at room temperature, just as most variable temperature studies refer to work under ambient pressure.

There are, however, several good reasons for having both temperature and pressure available as independent variables in a scientific study.

For example, materials exist in different phases under different pressure and temperature conditions. Usually, gas, liquid and at least one solid phase can be obtained under ambient pressures (even this is not always true c.f. liquid CO₂ or solid He) but all solids undergo transitions to other phases if the pressure and temperature conditions are adjusted appropriately. In order to be able to study these new phases, it is necessary to be able to produce the temperature and pressure conditions under which they can be formed. Not only are the new phases themselves of interest, but the transitions in which they are formed and the mechanisms by which the transitions proceed are also of considerable scientific interest. Some phase changes show transition lines on a temperature versus pressure phase diagram that are almost parallel to the pressure axis. These involve significant entropy change, negligible volume change, they are often considered to be "temperature driven" and are best studied in (various) fixed pressure variable temperature type experiments. Other transitions show transition lines almost parallel to the temperature axis, are "pressure driven", have significant volume changes across the boundary and are best studied by fixed temperature variable pressure experiments. Most phase transitions are part-way between the above two extremes and useful data can be obtained from both types of experiment.

As a spectroscopist, one is measuring peak position, band width, band shape, or intensity of features within a spectrum. The progressive changes in these parameters as a function of pressure or temperature within a single phase may well be as important in any one particular study as the more dramatic (often discontinuous) changes which take place at a transition.

It is essentially for the above reasons that we have concentrated our recent instrumental developments on variable temperature high pressure spectroscopic cells, within which the materials of interest can be studied systematically as a function of either temperature or pressure.

We are beginning some diamond anvil cell studies in order to reach higher pressures, and we are starting some high pressure X-ray studies to obtain the complementary data on unit cell dimensions.

However, the work reported here concentrates entirely on the lower pressure range spectroscopic studies. The object throughout this work has been to obtain high quality spectroscopic data from infrared, far infrared and Raman spectra of materials using temperature and pressure as accurately-measured independent variables.

In the past we have tended to concentrate our attention on work at temperatures below ambient and a significant fraction of the publications by the group refer to such work. During the period of the contract reported on here, our attention has turned towards higher temperature effects. We have become interested in the phenomenon of melting (i.e. the solid-liquid phase change) and have constructed a high pressure far infrared cell to study the far infrared "liquid lattice modes" reported for some liquids just above their melting temperatures. This cell is intended for use in the temperature range 200 + 600 K and for pressures up to 15 kbar. It is a fairly conventional intensifier type liquid cell for sample path lengths up to 3 cm with an optional inner cell for very short path lengths.

We have also developed an internally heated high pressure Raman cell that we have tested up to 1500 K and 5 kbar. It seems likely that a slightly modified design would allow us to work up to 2000 K and 10 kbar. However, by 1500 K the black-body emission from the sample and cell is several times larger than the Raman signal stimulated by 900 mw of 488 nm radiation. The use of pulsed and/or U.V. laser excitation will be needed to get good Raman signals from higher temperature samples.

The above two cells are described in some detail in the following section. After this, a section on the scientific results includes a subsection on the preliminary results obtained with the two cells developed during this period, and a subsection outlining the significance of the 55 publications by the group during the period of this contract.

2. High pressure apparatus

Our research group has a continuous programme of high pressure spectroscopic cell design and development, which has steadily increased the range of the experiments that we can undertake. During the period of this contract we have made significant progress on two cells: (i) a far infrared liquid cell of the intensifier type and (ii) a Raman cell of the internal-heater, gas-medium type. The development work on these cells is described below.

2(i) Far i.r. intensifier type cell

In order to understand the design of this cell, a brief

introduction must be given to the type of problem for which it was required.

We have become interested in the possibility of studying the phenomena of melting, crystallization and glass-formation using far infrared (and Raman) spectroscopic methods. In particular we wished to develop a cell within which we could study the effects of pressure on the far infrared spectra of selected materials just below and just above their melting points. Our attention had been drawn to the "liquid lattice modes" shown by some organic liquids. Thus, although our more general interest in melting and glass-formation is part of our high temperature interests, it was decided that the cell for this part of the study required the modest temperature capability of 200 - 600 K. The liquid (or soft solid) sample thickness should be adjusted during the setting-up procedure between about 0.01 cm and 3 cm. (This is because the features of interest in the spectrum of a pure material may be very strongly absorbing and require no more than a very thin sample, but we wish to study the effects of dilution within non-polar liquids where the effects quickly become very weak and much thicker samples are required.) The cell must function within a vacuum, (since far infrared instruments are evacuated to remove the very intense absorption of water vapour) and the cell must have windows of a reasonable size because of the low intensities of far infrared sources.

An intensifier type cell is essentially a double-ended piston, the large area end of which is subjected to modest oil pressure which drives the small area end into an enclosure containing the pressure transmitting fluid until a balance of forces is obtained. Thus, ignoring frictional forces, $P_1 A_1 = P_2 A_2$ or $P_2 = P_1 A_1 / A_2$, where P indicates the magnitude of pressure, A area, and subscripts 1 and 2 refer to the low and high pressure ends of the piston respectively.

Pressures up to about 1 kbar can be generated very easily with a simple hand-operated pump and thus a modest area ratio (A_1/A_2) is enough to allow pressures up to 15 kbar to be transmitted to the sample. We used an area ratio of about 20:1 in the cell described below.

In an intensifier type cell, the sample is mounted within the high pressure enclosure into which the high pressure end of the piston is driven. If, as in this case, it is desired to vary the temperature of the sample enclosure, then it is necessary to thermally isolate that part of the equipment, so that the low pressure part can be kept close to room temperature.

The following figures (and their lengthy legends) illustrate the important aspects of this cell design.

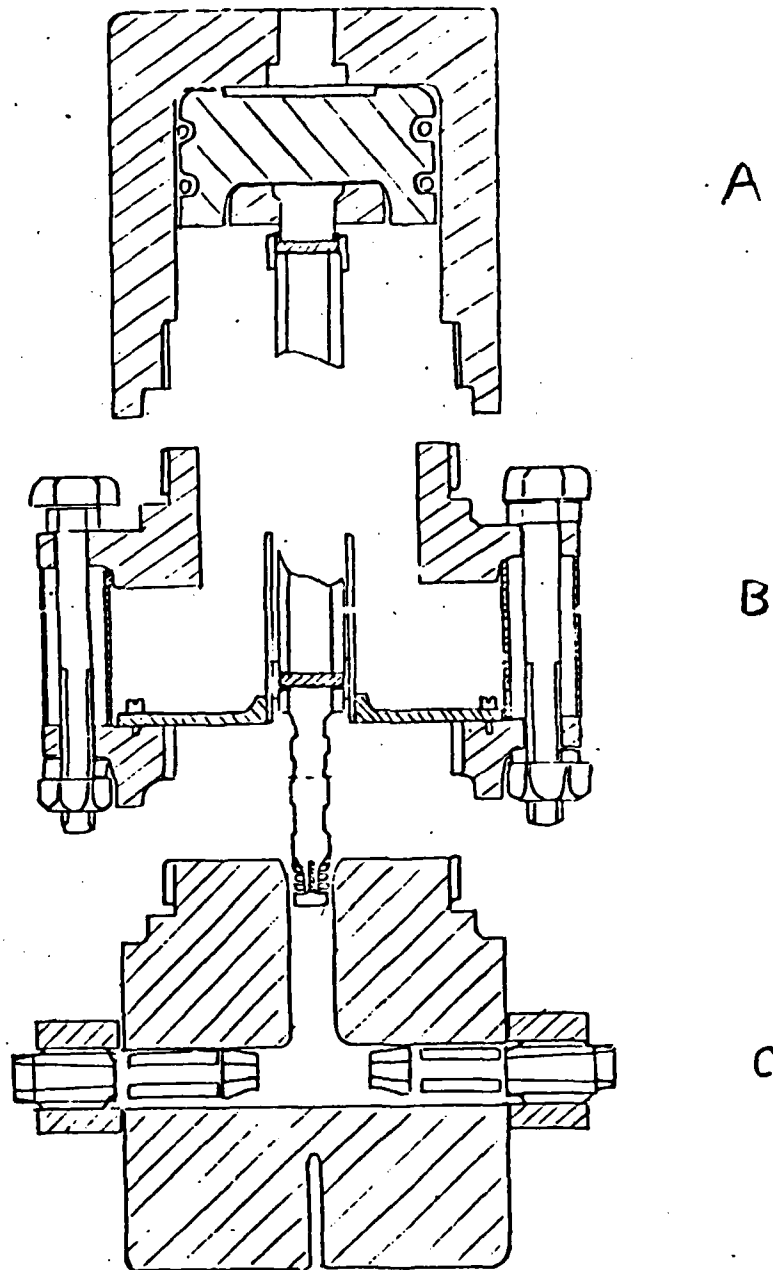
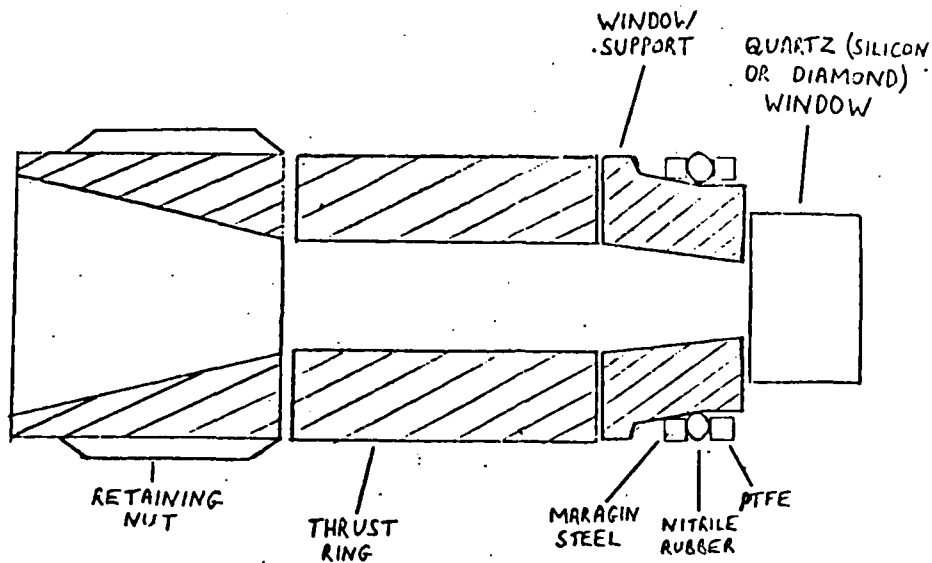


Fig.1 This shows a view of the far infrared intensifier cell. It clearly divides into three sections marked A,B & C. A is the low pressure ram, into the top of which oil is forced from a small hand pump. B is a thermal isolation stage, which for room-temperature work could be omitted. C is the high pressure part of the intensifier type cell.

CELL SEALS

WINDOW SUPPORT



PISTON

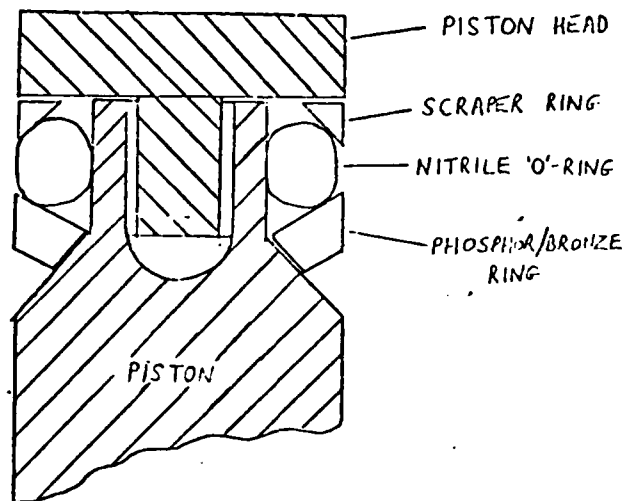


Fig.2 This shows details of the window support system and the piston head of the fig.1 cell. By using different length thrust rings and a small amount of adjustment on the retaining nuts, any required spacing (in the range .1mm-3cm) between the window inner surfaces can be obtained. The high pressure seal on the piston is made by the "O" ring and wedge-ring which is coated with PTFE. The piston head is necessary for the loading and more particularly the unloading of the piston seal.

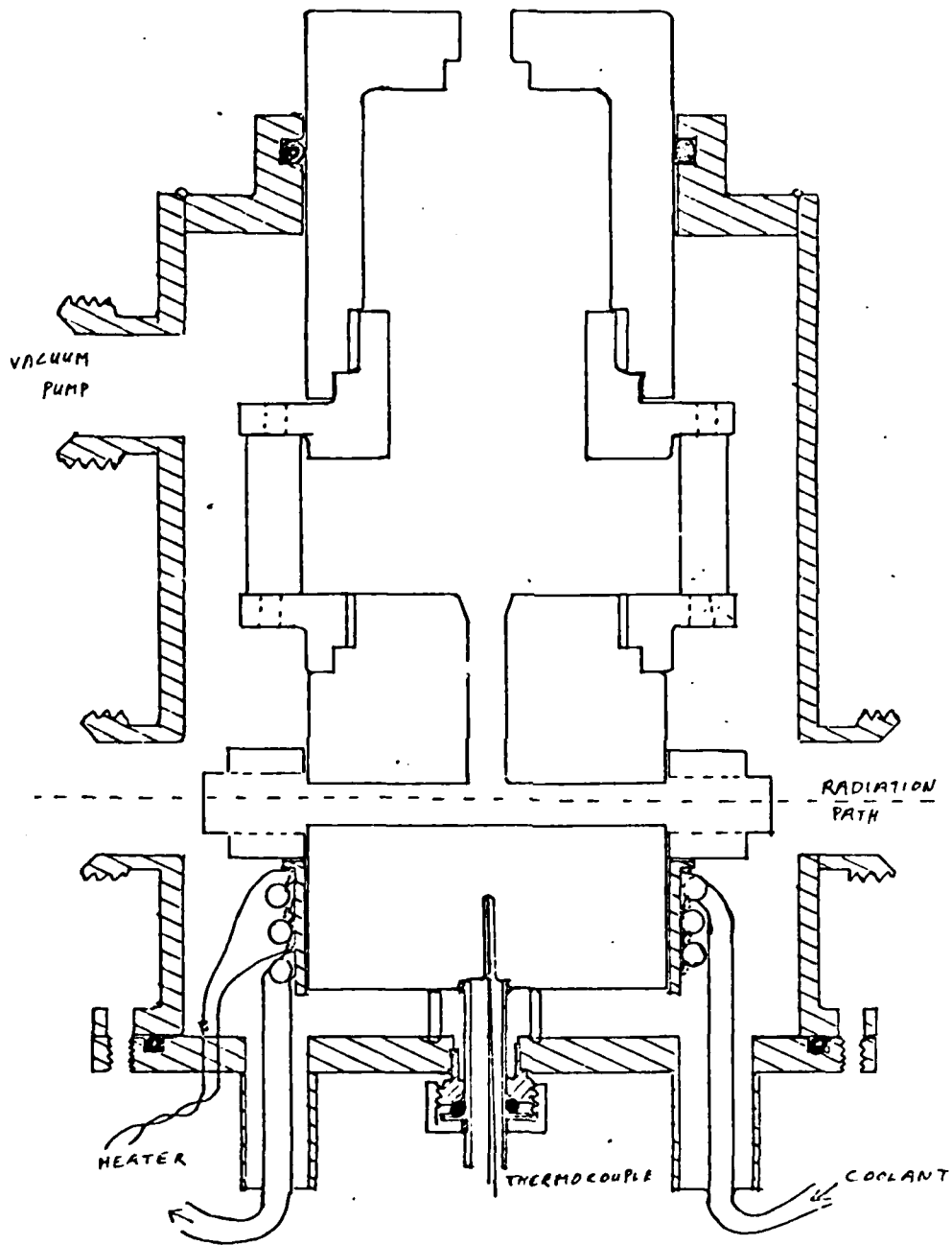


Fig.3 An outline of the intensifier type cell is shown here within its vacuum jacket. The heating or cooling support, within which the cell is a push fit is shown, as is the extension tube which is soldered to the base of the cell to allow the thermocouple to be at ambient pressure.

2(ii) Internally heated high pressure Raman cell for use
up to 1500 K

Laser heating of the tiny samples held within diamond anvil cells has allowed very high temperatures to be obtained under very high pressures. The work reported so far using that technique has been for transitory high temperatures (estimated rather than measured) used to trigger reactions or phase changes. It is not clear how easily that technique could be extended to provide access to the type of data that has been our main objective. That is, the systematic collection of accurate spectroscopic data as a function of temperature or pressure, where these two variable parameters are kept essentially independent of one another.

Our approach to the variable temperature, variable high pressure problem has allowed us to collect a large amount of informative data in the temperature range 6 K to 600 K. In considering the extension of our studies into a higher temperature range, we therefore decided to retain, as far as possible, the same approach. Thus in the cell described below, the pressure is transmitted to the sample by gas which is compressed by a separate compressor unit, (see Final Technical Report to ERO United States Army for grant number DA-ERO-76-6-054) and the high temperature is produced by electrical heating of a small tungsten wire element in the centre of the cell.

In this way the pressure and temperature can be adjusted in an essentially independent manner. There does remain a small interaction, i.e. increasing the temperature does tend to increase the pressure, but the heated volume is a small fraction of the total high pressure volume, so the effect is small and easily compensated.

The pressure is inevitably limited to that available from the compressor system, 14 kbar, but we have been concentrating on the high temperature aspects of the design and have not yet tested our prototype cell beyond 5 kbar. However there does not seem to be any insurmountable problem to fabricating the next cell in such a way as to withstand the full pressure available from the compressor.

Two modifications of the prototype cell described below have been tested so far. In its initial form, a radially supported, thick-walled sapphire cylinder was used (i) to support most of the pressure, (ii) to act as the high pressure windows and (iii) to drop the central high temperature down to the 750 K that the maraging steel outer cell could withstand without rapid deterioration.

The major problem with this version of the cell was the design of an adequate heater element to fit within the 2 mm dia-

meter internal bore of the sapphire cylinder. Up to sample temperatures of about 800 K at pressures up to 5 kbar this form of the cell functioned quite well. However, attempts to raise the temperature much higher than this (i.e. establish a large radial thermal gradient across the sapphire cylinder) were unsuccessful. The main reason for this seems to have been the high thermal conductivity of the sapphire relative to that of the pressure transmitting medium. Whilst the entire sapphire cylinder could be allowed to heat up almost uniformly (i.e. for $T < 750$ K, the limit imposed by the maraging steel outer cell) there was no problem. For higher sample temperatures the outer surfaces of the sapphire still had to be held down to 750 K, although the inner surface had to be heated significantly above that. The heat-flow problem then established a large temperature gradient across the pressure transmitting medium and the heater element temperature had to rise much faster than the sample temperature. Efforts to raise the sample temperature much beyond 800 K invariably caused the heater to burn out fairly quickly. Also, the single crystal sapphire (C-axis along cylinder axis) did not like the combination of radial temperature gradient and radial pressure gradient and it tended to fracture after a relatively short time under those conditions.

Thus, after trying different heater configurations and different radial and longitudinal sapphire support, it was decided to try a second modification.

In this second form, a short length of quartz tube mounted within pyrophyllite was used to replace the thick-walled sapphire cylinder. The same maraging steel cell was used, since it was available together with its cooling jacket and the alignment mounts for positioning it in front of the Raman spectrometer. It has become clear that a more convenient cell could be designed round this second furnace system. However even with the present system it has been possible to record Raman spectra from samples under pressures up to 3 kbar at temperatures up to 1500 K.

The fused quartz tube in the present cell has dimensions of about 4 mm long, 2.5 mm internal diameter and 4.05 mm outside diameter. High pressure gas is allowed to entirely surround the quartz tube which is not subjected to any direct mechanical stress. A relatively small thermal gradient will be established across the quartz when high sample temperatures are required, but the major part of the temperature gradient between the sample and the steel outer-cell will appear across the pyrophyllite (or Agalain) spacer between the quartz and the steel. The thermal gradients along the light paths (laser in, laser out and Raman signal out,) are established across the pressure-transmitting gas which fills the space between the quartz tube and the pressure-retaining windows, (sapphire). This design was chosen after the previous modification of the cell failed essentially because of the large thermal gradient that the high pressure gas was found to support.

In our Raman system signal optical axis is ho seems to be quite stable below) and Raman out (hor ance in the temperature-i instability in the laser-experiments we have made (e.g. change dimensions o benefits of changing the a horizontal plane. Ther or reduced heat flow adva approach.

The figures below an of the significant points the modifications describ

3. Scientific studies

In the previous sect pressure spectroscopic ce definitive work has yet b liminary results are avai other of them.

Although this data i particular relevance to t fore be briefly described this, a further subsectio significance of the work tions is outlined.

3(i) Far infrared "liqui

The proposal investi modes (0 to 200 cm^{-1} say) persist in a somewhat mod be studied to ascertain t liquid and liquid-solid p

Our more general int glass-formation (and the is in materials with fair reported examples(1)(2) o materials with melting po

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- (1) G W Chantry; IEEE Tr
 - (2) E Knozinger, D Leutl

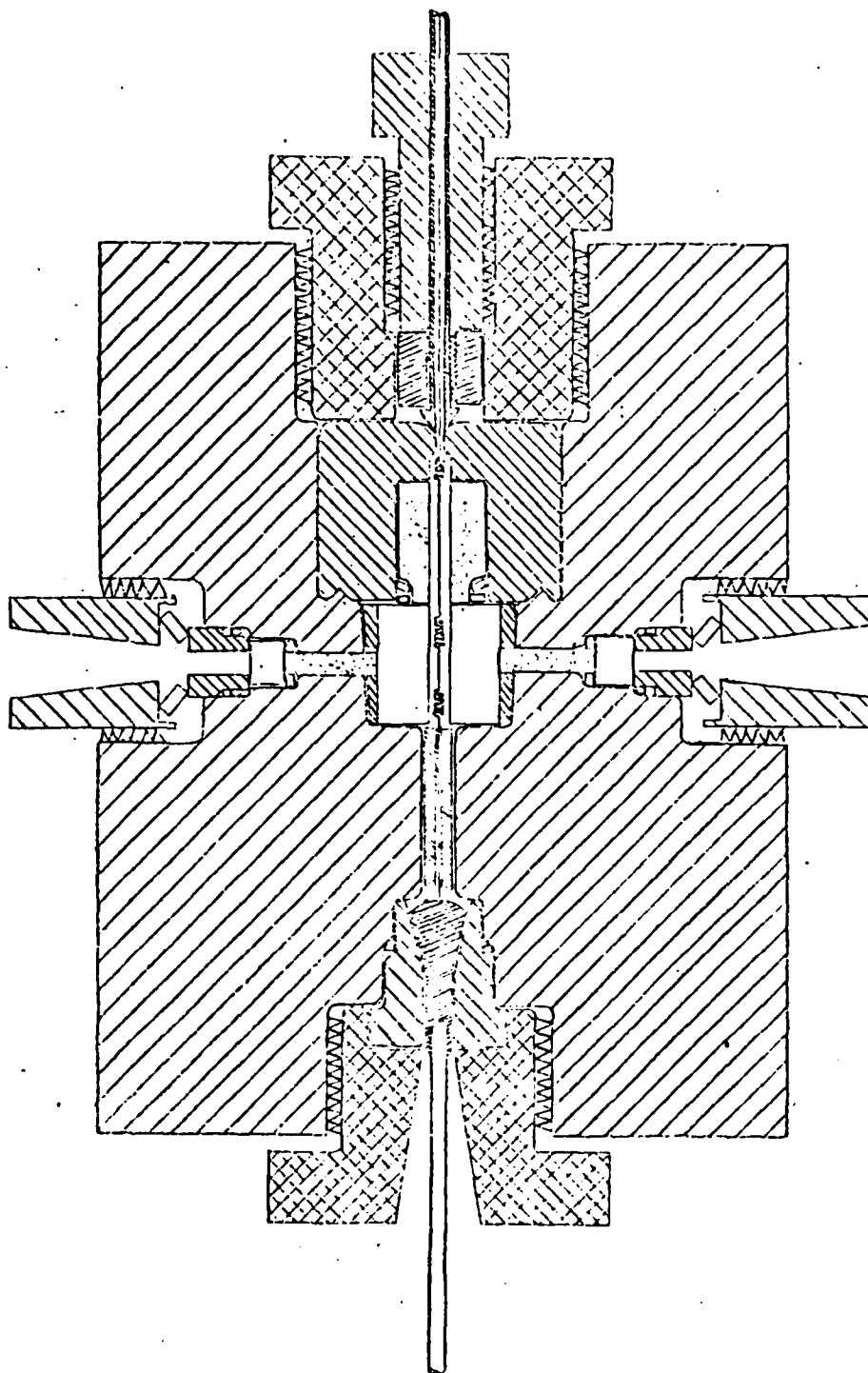


Fig. 4 This shows the high temperature, high pressure Raman cell in its initial form. The radially supported sapphire cylinder in the centre of the cell was of length 10mm, OD 12mm and ID 2mm. Sodium chloride was pressed into the window supports (completing the cylindrical support of the sapphire) and the small outer sapphire windows could move back against Bellville spring supports if expansion of the NaCl demanded this. The windows shown here are the "laser in" and "laser out" windows, with a similar (but smaller F no.) window in the other plane for collecting the Raman signal at 90°.

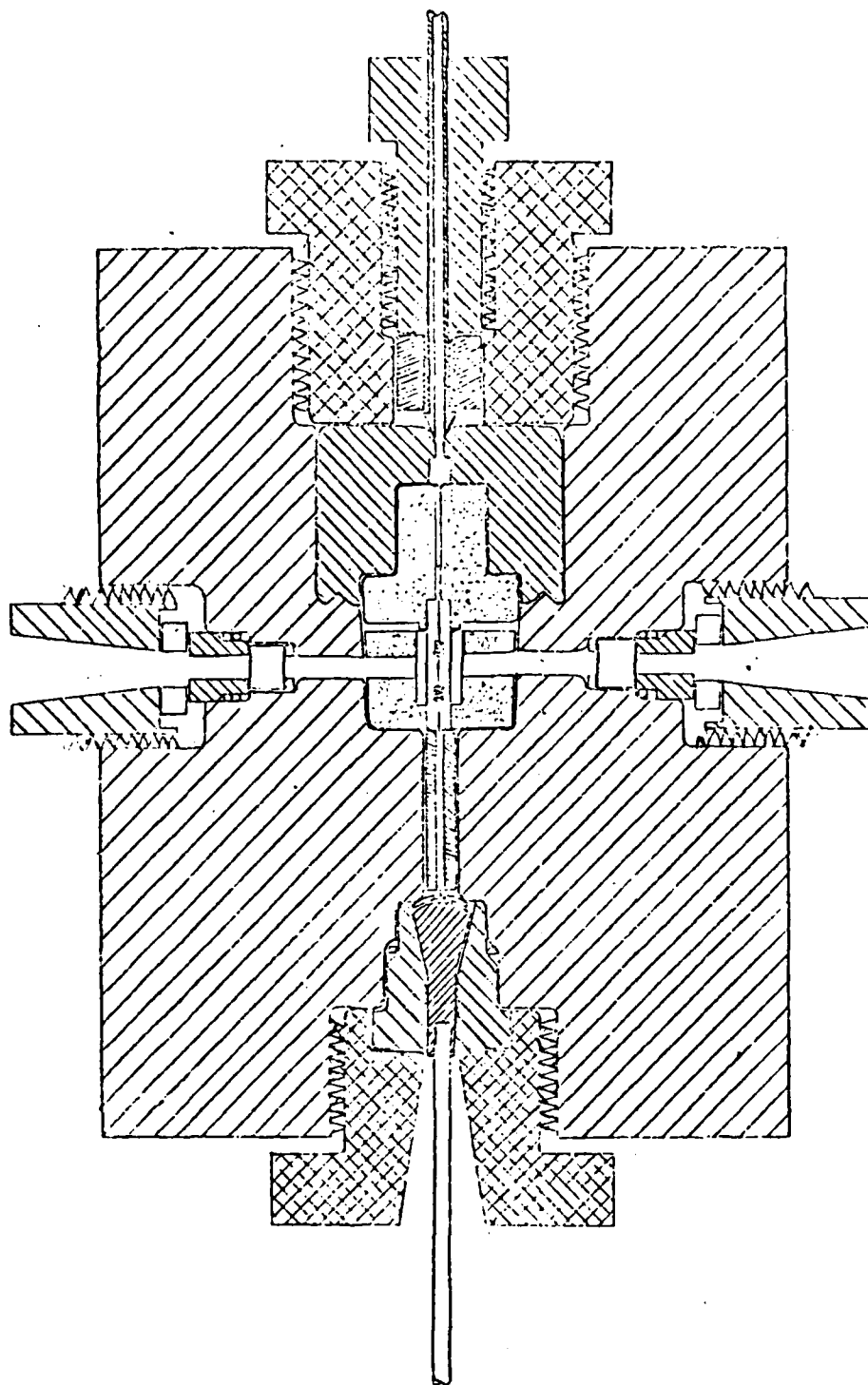
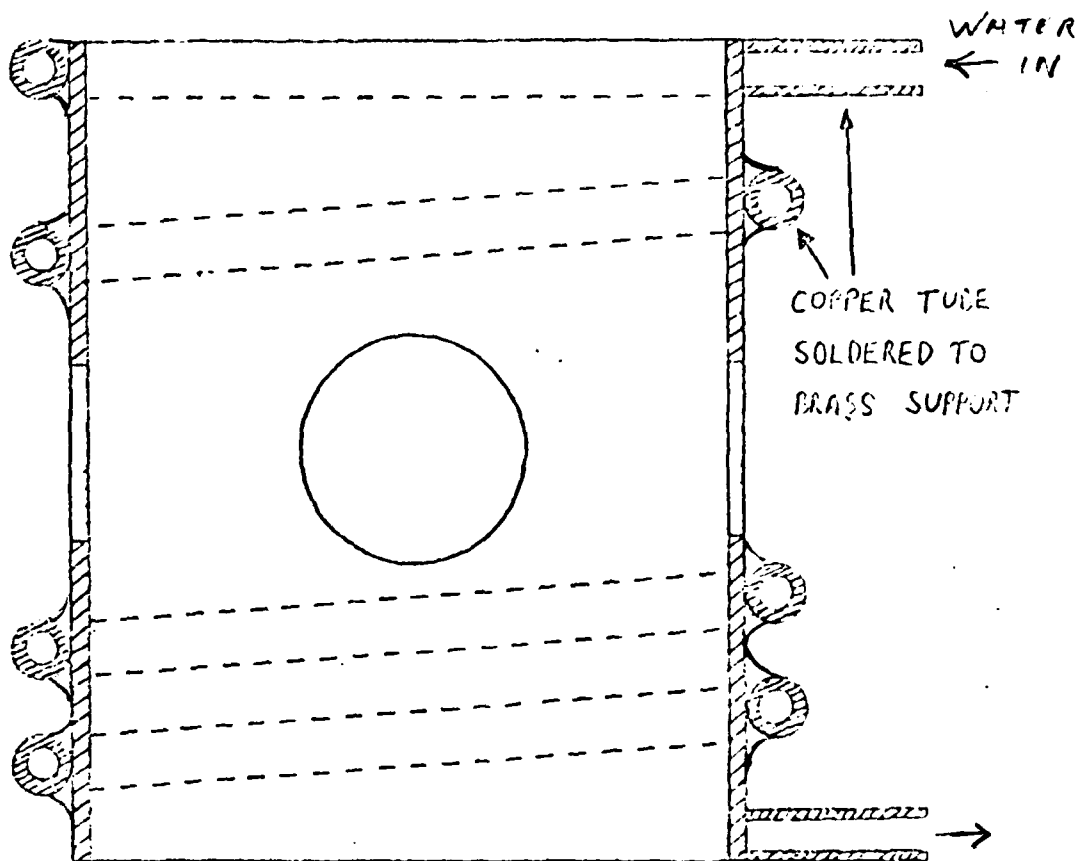


Fig.5 This shows the later modification of the high temperature high pressure cell in which the central optical component is a fused quartz tube, length about 5mm, OD about 4.05mm and ID about 2.5mm. The high pressure gas completely surrounds this inner cylinder and the full pressure is taken on the outer sapphire windows. Although not fitting well enough to form a high pressure seal, the Agalain insulation is tightly fitted to the quartz tube and stops any tendency of the high temperature gas to circulate beyond the central region.



COOLING JACKET

Fig.6 The cooling jacket is simply a tight fitting brass sleeve for the cell (which is pushed over the cell before the window supports are screwed in) round which copper tube has been soldered. Cooling water is passed through the copper tubing.

constructed the far i.r. intensifier type cell described above in section 2(i), with a temperature range of 200 K + 600 K and a pressure range up to 15 kbar, as a reasonable compromise to start this study.

The instantaneous short-range order in liquids just above their melting point is known from radial distribution function measurements to be similar to that which exists in the solid. However, the stability of that local order, expressible in terms of mean lifetimes of aggregates of various sizes, is poorly understood. Crystallisation from the melt may be expected if the temperature and pressure conditions allow one of these aggregates to exceed a certain critical size. The "liquid lattice" modes that we set out to study, are probably best visualised as the intermolecular modes of the sub-critical crystallites. Where a sub-critical crystallite is the term used to describe an aggregate within the liquid which has a lifetime that is long compared with that of the "liquid phonon".

Any spectroscopic observation of liquid lattice effects must be expected to show broad bands (i) because of the short lifetime that must be expected for any particular vibrational state of such a system and (ii) because any observation must represent an average effect which can be regarded as an integral across the appropriate distribution of sub-critical crystallites of different sizes.

In fact there is reason to believe that close to crystallisation the observations will be dominated by effects due to crystallites close to a specific sub-critical size, since this would seem to produce the energetically most favoured configuration. If this size of sub-critical crystallite has dimensions that are larger than the mean free path of phonons in the solid just below the melting point, then the spectra of the melt can be expected to closely resemble the spectra of the almost-melting solid. Under these conditions one might expect to observe the "liquid-lattice" modes, which could reasonably be interpreted in a manner closely analogous to that used for the solid.

Glass formation occurs when competing structures (of* similar energies) inhibit the growth of long range order of any one type. The simplest situation to envisage is where two competing structures produce within the melt, approximately equal numbers of sub-critical size crystallites. If these crystallites are such as to show the above liquid lattice effects, then the spectra obtained from the melt should show evidence of bands originating from the two structures. Pressure is expected to influence the relative stability of different structures. It is reasonable to assume therefore that the study of the "liquid lattice" modes of appropriate systems as a function of pressure will indicate clearly the conditions when the melt will crystallise into one or other structure or undergo

* Difference in energy/molecule small compared with kT , where T is the temperature of the glass transition.

a hardening into a glass.

It is our intention to investigate the validity of the above ideas, and the cell described in section 2(i) was constructed for that purpose.

So far we have recorded survey spectra for a variety of systems and some preliminary high pressure data for t-butyl cyanide, acetone and acetonitrile. This work has been briefly described in one of our recent publications, (Temperature and pressure effects on the far i.r. spectra associated with liquid lattices. M J Baker, W F Sherman and G R Wilkinson *J.Mol.Str.* 115, 311, (1984),) but the data so far available allows us to conclude no more than that it is consistent with the concept of similar vibrational modes in liquid and solid phases close to the melting point.

A change over in personnel within the group has unfortunately held up this work, but we are now almost ready to resume work on this part of our programme.

3(ii) High temperature high pressure Raman study

Although many man-hours have gone into the development work on the high temperature high pressure Raman cell described in section 2(ii), we have not yet seriously attempted any definitive scientific work with that cell. However two types of sample have been studied during the evaluation and development work, and some description of the data obtained should be given here.

When the first modification of the cell was pressure tested up to 5 kbar, nitrogen gas was used. However the Raman spectrum of nitrogen gas under 5 kbar pressure is at first sight relatively uninformative. For example, all sign of rotational structure has disappeared before the pressure reaches 1 kbar, and by 5 kbar the low frequency Raman spectrum is little more than a liquid-like wing on the side of the laser exciting line. We did not feel justified in using the nitrogen Stokes to anti-Stokes intensity ratio to measure our temperatures, because the spectrum was too similar in shape to the instrumentally produced wing of the intensely scattered laser line itself. In fact we showed later that for Raman shifts greater than about 30 cm^{-1} , the wing of the Rayleigh scattered laser was negligible under those conditions.

However, at that stage in our evaluation of the cell we took no more than a brief look at the Raman spectrum of N_2 under pressures up to 5 kbar and temperatures up to about 800 K. We turned our attention to H_2 , which, because of its wide-spaced rotational bands was (i) likely to retain identifiable single components up to much higher temperatures and pressures and (ii) was likely to yield more precise temperature measurements at high temperatures.

In the 4th periodic report on this contract (covering the dates August 1982 to February 1983) we showed some of our rotational Raman spectra (Stokes and anti-Stokes) and Q branch components of the Stokes vibration-rotation band near 4150 cm^{-1} for molecular hydrogen under 1.5 kbar pressure and temperatures up to 800 K. We still hope to analyse this data more carefully as indicated in the 4th periodic report, but this is not at present a particular interest of any member of our group and we have been concentrating on other aspects of our work, as shown by the list of publications at the end of this report.

Although the hydrogen spectrum proved to be a convenient way of measuring the temperature within the cell, that method was stopped when the maraging steel support cell developed a crack that was almost certainly caused by hydrogen embrittlement. (We also had a component within our compressor system fail for a similar reason at about the same time.) However, the hydrogen work had allowed us to study the shape and intensity of the Rayleigh wing under the conditions of temperature, pressure, laser power and spectrometer slit width that we would expect to work and this indicated that for Raman shifts greater than 30 cm^{-1} we could ignore the contribution from the Rayleigh wing.

Thus when we restarted this study with a second cell of the same design we felt reasonably confident that we could measure the temperature reliably (although not with very great precision) by measuring the ratio of the Stokes to anti-Stokes intensities in the Nitrogen spectrum.

It was during this phase of the work that it became apparent that for temperatures above 800 K at the bore of the sapphire, the sapphire conducted the heat too efficiently to the steel support which was held at an estimated 700 K. After experimenting with various heater designs we concluded that sample temperatures above 800 K were going to require some lower conductivity material between the central region of the cell and the maraging steel support cell. We did contemplate making the steel support cell from a high temperature steel, but ultimately we would have reached the same problem of too great a heat flow through the sapphire. Thus the second modification described in 2(ii) was developed, and temperatures of the order of 1500 K were achieved within the high pressure enclosure.

Our main interests have been in solid state samples and we wished to test the ability of the cell to provide data on such samples under high temperature and high pressure conditions. We have so far made measurements on one material, crystalline quartz. This material was chosen as a sample because it had one well-studied

phase transition ($\alpha \rightarrow \beta$) which is reported to be very sensitive to pressure, and another less well documented transition within our temperature and pressure ranges. Also, the strongest band in the Raman spectrum of quartz is at about 460 cm^{-1} , and this remains true up to 1500 K. Although a Raman shift of 460 cm^{-1} is not ideal for Stokes:anti-Stokes temperature measurement at about 1500 K, it is still possible to obtain reasonably reliable values for temperatures in this way.

Fig.(7) below shows parts of the Stokes spectrum of quartz at a temperature of about 1400 K and a pressure of 1.8 kbar. We were concerned about the temperature capability of the cell at the time that this work was carried out and were using the minimum pressure that we felt was consistent with a realistic test of the cell. Having proved to our satisfaction that the system can generate these temperatures we can turn our attention to the careful control and measurement of both temperature and pressure, and begin the scientific part of this project.

The time-scale for high pressure research is such that the development of new equipment to the point where it becomes scientifically useful is usually greater than the period of a grant or contract. This has proved to be true for the present contract in that during the past 2½ years we have brought two new cells up to the point where they have become scientifically useful, but we have not yet had time to make good scientific use of them. However the scientific (as opposed to instrumental) aspects of our work have continued during this time, making use of the equipment developed earlier. (e.g. the work done under grant DA-ERO-76-G-054). This is clearly shown by the 55 publications listed at the end of this report.

In the following subsection, a brief overview is given of the work described in the list of publications.

3(iii) Overview of publications

The 55 publications are grouped under sub-headings, so that those carrying specific types of information can be more readily identified

3(iii)(a) Review papers

Two review papers, refs. 23 and 51, have been published as the written equivalents of invited conference papers in which the recent work of our group was put in the wider context of "I.R. and Raman spectroscopy at high pressure".

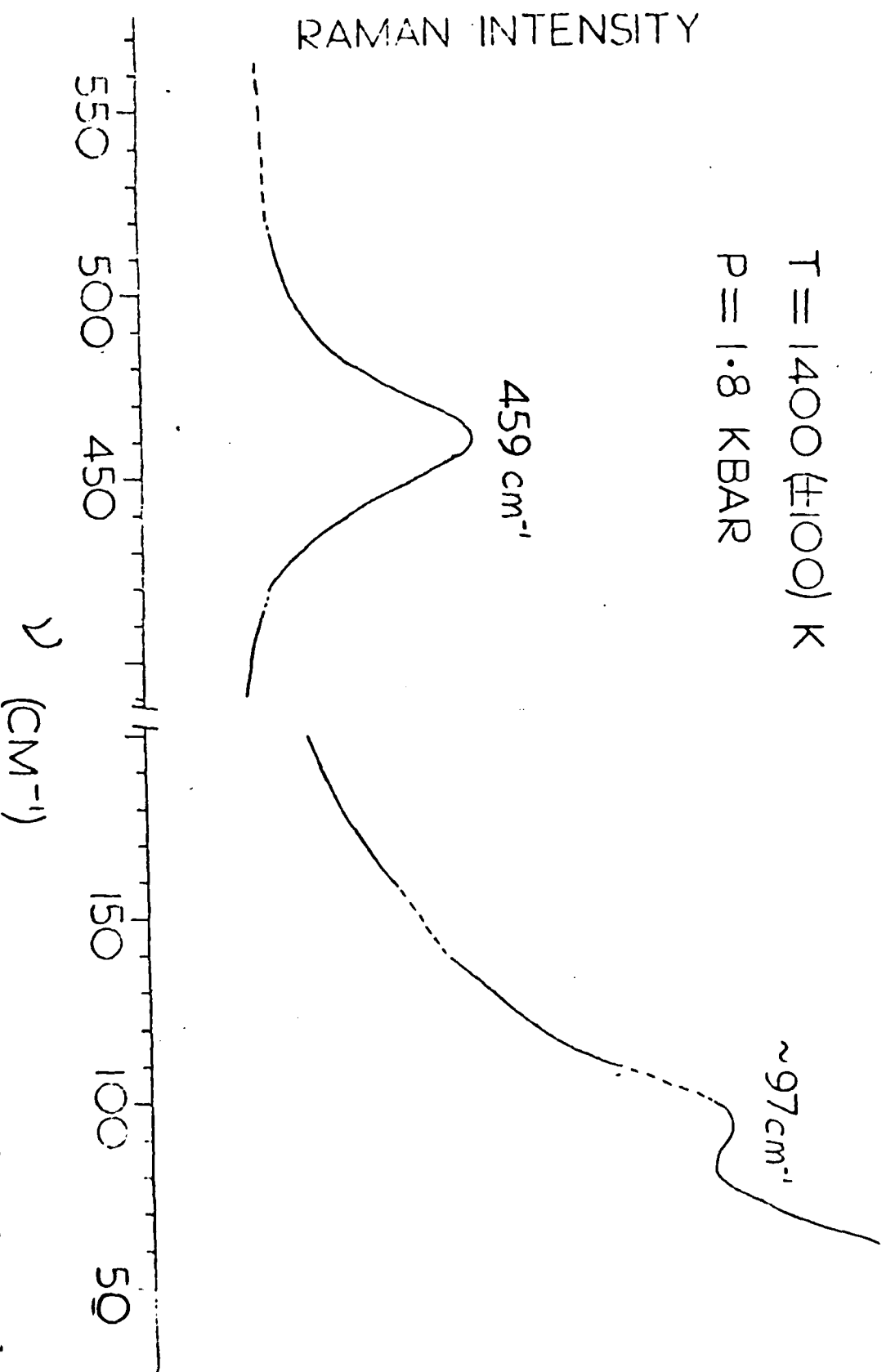


Fig. 7 This shows part of the Stokes Raman spectrum of a quartz sample which had been heated several times above 1000K under 1.8 kbar. The sample had become badly cracked by this stage and although the band at 459 cm^{-1} was still clear enough to be used as a thermometer, the only other band visible was that at 97 cm^{-1} (the 127 cm^{-1} band under ambient conditions) and that was difficult to measure because of the strong laser wing caused mainly by the cracking of the sample.

3(iii)(b) Impurity ions in alkali halides

This is the biggest single group of papers, there having been 15 publications on this topic during the period of this contract. (Refs.No. 1, 2, 5, 7, 10, 11, 25, 33, 35, 42, 44, 47, 48, 53, 55.)

By isolating an ion within a well-defined crystalline environment, (which does not itself have a very extensive spectrum) the spectroscopic properties of the ion become very clearly defined, and the samples are easily handled. Thus, alkali halide/impurity ion crystals are, for many purposes, model systems. The spectra are relatively easily interpreted, the effects of temperature and/or pressure changes are usually unambiguous.

In the publications listed here, we have used these model systems to improve our understanding of: (i) the effect of the geometry of the environment, (NaCl and CsCl structures are available) (ii) the effect of changing the geometry of the environment (pressure induced phase changes of the NaCl to CsCl type) (iii) Fermi resonance (an effect present in virtually all spectra, but often ignored because of the difficulty of unambiguously identifying the consequences) (iv) lattice side bands on vibrational modes, (again present in virtually all solid state spectra, and again usually ignored) (v) hydrogen bonding (vi) resonance Raman (vii) effects of temperature and pressure changes within a single phase.

Systems of this type have been of interest to us for over 25 years now, but there are still many aspects of their vibrational properties that have not been fully explained. The relative simplicity of the spectra shown by these systems has however allowed effects to be clearly identified and interpreted for these systems before the analogous, but more complex effects have been explained for other systems. Although we do not have many more experiments currently planned for systems of this type, it would be surprising if we did not return to them later.

3(iii)(c) Torsional modes

Four publications (refs. 3, 4, 26 and 34) are concerned with the temperature and pressure dependences of torsional modes.

We are interested in the intermolecular forces that are operative in determining the positioning of molecular groups within solid state samples. Clearly, those which determine the orientation of small molecular groups which might otherwise be (relatively) free to rotate have a somewhat special place, and a series of specialised techniques have been developed for studying the effects they produce. Dr. Ratcliffe, who joined our group for a year, is an expert on torsional motion in condensed phases and

the papers in this sub-section describe some of the work that he performed here at King's College.

3(iii)(d) Layer compounds

Four of our recent publications (Refs.6,8,22,24) have been concerned with the Raman spectroscopy of "layer compounds". The strong intralayer and relatively weak interlayer interactions make these compounds attractive materials for the study of inter-molecular interactions.

3(iii)(e) Inorganic crystals

Work under this heading can be subdivided in several ways. For example eight publications (Refs. 12,27,28,36,45,50,52,54) are largely concerned with lattice dynamical calculations; four (Refs. 9,15,31,39) are concerned with pure crystals containing small poly-atomic ions which have previously been studied as isolated species within alkali halides and one (Ref.20) concerns the pressure dependence of the alkali halide TO modes. They have in common the search for the simplest forms of reliable interaction functions.

3(iii)(f) Instrumental

Two of our publications (Refs.13,21) are primarily concerned with instrumental advances. They describe different aspects of our work in bringing our far I.R. interferometers under microcomputer control.

3(iii)(g) Ice

We have been engaged on a detailed study of the Raman spectra of different ice polymorphs in their regions of true thermodynamic stability. Three of our recent publications (Refs.14,46,49) have described different aspects of that work.

3(iii)(h) Organic crystals

We have had a long-term interest in organic crystals where some simplifying characteristic of their structures have brought them within the range of the quantitative type of study that we favour. The materials discussed above in subsection 3(iii)(c) also belong under the present sub-heading and Refs.17 and 32 are further examples of this type of work.

3(iii)(i) Theoretical

All our publications are aimed at improving our understanding of the theory of our subject but in most cases the major emphasis has been on the interpretation of new experimental results. However several of our papers (Refs.19,30,41,43 and most of those in subsection 3(iii)(e) are quite clearly of a theoretical nature.

3(iii)(j) Others

Six publications have not yet been mentioned and although they do not have any clear reason for being grouped together they(16,38) have been put within this final category. Two of these papers are concerned with tetrahedral ions in solution, two describe the far(37,40) infrared "liquid lattice" work, one describes a variable pressure(29) and temperature study of the Raman of quartz and one describes a collaborative project in which some of our high pressure optical cell equipment was used to study the Brillouin scattering from ammonium halides in their transition regions.(18)

4 Conclusions

This contract was for the use of spectroscopic techniques to probe material held under high pressure at various temperatures for the purpose of improving our understanding of intermolecular forces and the properties of materials that depend upon them. To include the development of new high pressure optical cells to extend our experimental capabilities to high temperatures (1500 K) and to investigate the possible use of non-spectroscopic probes for the study of basic properties of materials under extremes of temperature and pressure.

The list in the following section of 55 publications by the group during the period of this contract (and the brief discussion of them given in the previous section) unambiguously shows the extent to which we have fulfilled the first requirement of the contract.

New high pressure optical cells have been developed with the aid of this contract, as discussed in the early part of this report, and we have managed to reach steady state conditions of 1500 K and 1.8 kbar. This development work will be continued and scientific studies using this equipment should begin very soon now.

In our consideration of non-spectroscopic probes, we concluded that X-ray data would be the most informative for our purposes and we have developed two X-ray cells which we hope to start using in the near future. (c.f. contract DAJA45-83-C-0031).

Thus we feel that we have fully completed the work scheduled under this contract.

It will be apparent that the above work has been completed as part of an on-going series of experimental and theoretical studies that have contributed substantially to our understanding of intermolecular forces.

We gratefully acknowledge that much of this work could not have been carried out without the financial support that we have received from the U.S. Army.

5. Publications

The publications produced by our research group have been listed in the periodic reports (1) to (6) submitted at approximately six-monthly intervals as required by the contract. However, they have been collected together into one list, which is given below.

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